Time resolved observation of multiple electronic configurations in the electronic relaxation of isolated molecules by photoelectron imaging

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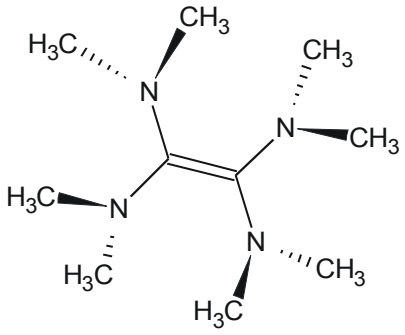
Abstract.: Femtosecond time resolved photoelectron imaging has been applied to the electronic relaxation of an ethylene-like molecule, tetrakis dimethylamino ethylene, excited to a $\pi\pi^*$ valence state. This method has an unprecedented efficiency for the observation of the states traversed by the wavepacket created on the initial state. We infer here that electronic relaxation gains efficiency by the mediation of nearby Rydberg states present at this excitation energy. The bulkiness of the molecule allows also the observation of an oscillatory wavepacket movement created on coordinates perpendicular to the relaxation coordinates.

INTRODUCTION

Molecules rarely reemit from the initially excited level after the absorption of a photon and if the molecule is sufficiently complex, light emission, a slow process, is not the main decay channel for the excited state. This relaxation, rapid in general, is essential to maintaining life, since our biological memory, DNA is continuously exposed to light and photochemistry can be harmful to it(1). The electronic energy is rapidly degraded and thermalised within the ground electronic state of these systems, preventing most of the photochemistry. These properties arise from the coupling (essentially non adiabatic) between the electronic configurations of the molecular systems accessible by optical excitation, and the others configurations. The mechanism which can allow an extremely fast relaxation in molecules, involves crossing between surfaces, conical intersections connecting the relevant excited states. It thus yields a direct descent to the lowest energy surface guided by the gradients along these surfaces. However recent discussions(2) show that the conical intersection is a complex process where the descending wave packet can be reflected, which has the effect of lengthening the relaxation time. Hence the relaxation mechanisms can become slow if the non adiabatic coupling between the intersecting surfaces is not too important. In order to maintain a generally fast decay rate there must exist a complementary, general mechanism for a variety of molecules. We propose here that such a mechanism exists and involves mediating states or surfaces allowing a more direct connection between the relevant excited surfaces. We report here its observation on a case molecule, a substituted ethylene, tetrakis dimethylamino ethylene (TDMAE). TDMAE has been excited by a femtosecond laser (pump) in the UV at 266 nm and the relaxation has been followed by a second femtosecond laser (probe) that probes the evolution by photoelectron spectroscopy. The probe laser ionises the TDMAE molecule and the resulting photoelectron spectrum is a fingerprint of the evolution of its electronic configuration(3, 4). For each

traversed electronic state there will be a different electronic spectrum indicative of the energy of the electronic state and its nature : valence, Rydberg etc. The TDMAE molecule was selected for its reported low ionisation energy, 5.4 eV(5), due to charge delocalisation over the dimethyl-amino groups and for its electronic relaxation properties frequent in ethylenic compounds (6, 7).



IP=5.4 eV

FIGURE 1: the TDMAE molecule.

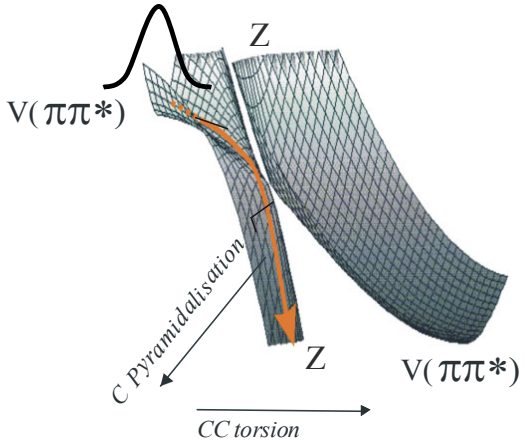


FIGURE 2 : schematic V(ππ*)-Z surface crossing inTDMAE

METHODOLOGY

The time resolved photoelectron spectra have been recorded in a special spectrometer with high collection efficiency: an ion velocity imaging device(8), used here for electrons. The instant ionisation creates an expanding sphere of electrons which is projected on a position sensitive MCP . The emitted electrons excite a phosphor and the image is captured by a CCD sensor. Electrons of increasing kinetic energies correspond to spheres of increasing sizes. The electrons are created by a combination of the pump (266 nm) and probe lasers (400 nm or 800 nm) exciting a supersonic beam of TDMAE seeded in helium. The images are created for each delay and stored after accumulation over several laser shots (~5000).

ULTRAFAST DECAY

We have reported in a previous paper the mechanisms of the electronic relaxation of free TDMAE, from the very initial step in the Frank-Condon zone, down to a fluorescent state, over widely different time scales, from the femtosecond to nanosecond times, as observed by ion and fluorescence detection(6). We have described these relaxation pathways in terms of generic properties in the excited states of double bond molecules exemplified by ethylene. With a femtosecond pump at 266 nm (4.6 eV), a wavepacket is formed that initiates a rapid downhill movement along the slopes of the excited potential energy surface. The wavepacket prepares initially a near planar geometry of the molecule with a valence configuration V($\pi\pi^*$ or $C^{\bullet}$- $C^{\bullet}$) which evolves to a state assigned with a zwitterionic character Z (C^+C^-). Subsequent relaxation with a 120 ps time constant occurs, in this scheme, to a charge transfer state CT. This latter state has the positive charge delocalised on the dimethylamino groups. This decay was observed through ion detection at the mass of $TDMAE^+$.

TIME RESOLVED PHOTOELECTRON SPECTRA

The ion velocity imaging technique is perfectly adapted to femtosecond time dependent photoelectron spectroscopy: very high sensitivity where the electron counting rate is very similar to that of the corresponding

ion(4). The energy resolution of the device is fully compatible with the frequency spread of 50 fs Gaussian pulses, i.e. 0.04eV and in addition the technique yields another dimension, the angular distribution of the electrons with respect to the ionising laser field. This information upon the angular distribution of the ejected electrons, although complex, since it depends upon many parameters, can yield additional information essential to decipher the evolution of the excited system through electronic configurations.

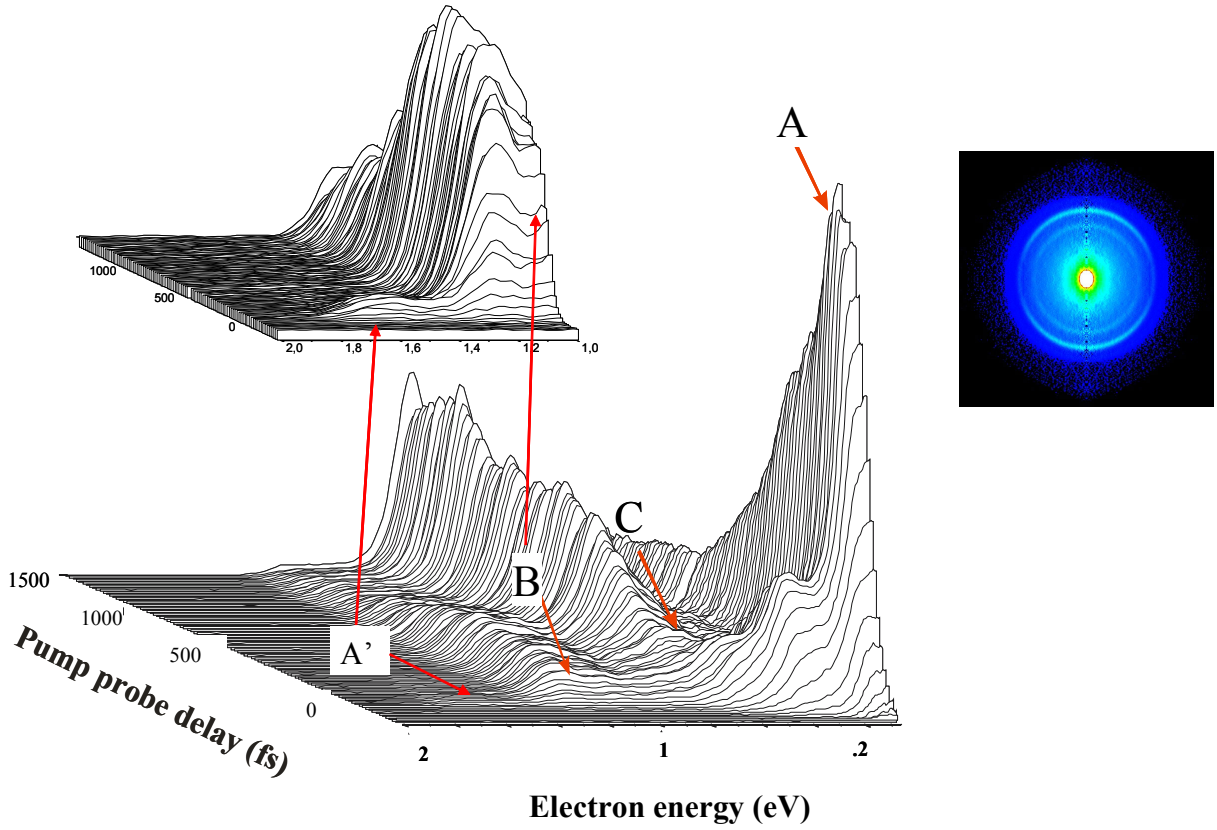


FIGURE 3:-Radially integrated electron velocity images of TDMAE excited at 266 nm and ionised at 800 nm. Each curve corresponds to a pump/probe time delay. The top insert is a magnification of bands A'and B. The insert on the right is the complete electron velocity image, but time integrated.

The spectrum shown in figure 3 is obtained from the images through the radial integration of the images for various time delays between the 266 nm pump and 800 nm probe. A typical image is shown in the right insert of figure 3. Four groups of bands can be seen in figure 3, only one of which is weak, A' and is magnified on top of the figure. The first, A, is close to the zero of energy of the electrons, with shoulders extending to 0.6 eV. The cumulated energy of the pump and probe lasers is 6.2 eV, which allows disposal of a maximum 0.8 eV for the electrons, with the 5.4 eV(5) ionisation potential of TDMAE. Therefore any band beyond the shoulders of A will involve a two photon ionisation which is reasonable given the intensity of the probe (~100 μJ).

These bands exhibit different time evolutions: peak A (maximum) decays exponentially in 200 fs, after being populated within the laser cross correlation time. It is then followed by a small plateau (5%). Peak B rises in 200 fs, as is clearly apparent in figure 3, from the band position, retardated with respect to band A, and decays in 400 fs. Finally, the decay of B is accompanied by the rise of C. An additional peak A' can bee seen at 1.6 eV that mimics A, it is clearly the two photon equivalent of A (one 800 nm photon = 1.55 eV) , as is verified below in figure 4. Measurements have been taken at longer times and reveal that band C can be identified with the formerly detected long lived state with a 100 ps lifetime, assigned to the Z state(6). The sequential decay which is apparent here, through the observation band B, reveals the existence of a new transient not detected by the observation of $TDMAE^+$

ions. We suspect (see below) that this state belongs to a Rydberg series converging to the adiabatic ionisation potential at 5.4 eV. The assignment of these three bands A, B, C to different electronic states (configurations) is further supported by polarisation measurements where the angular distribution of the electrons with respect to the ionisation laser is recorded. It appears that each band can be associated with a constant polarisation, characteristic of an electronic state.

The first Rydberg state of the TDMAE molecule observed in the absorption spectrum at 400 nm (5, 6), is a weak feature, which was assigned as belonging to the ns Rydberg series converging to the ionisation limit at 5.4 eV. This limit is very diffuse and the ionisation efficiency passed this threshold grows steadily until 6 eV. The weak appearance of this band and the very diffuse onset of the ionisation should relate to a disfavoured geometry of the ground state $TDMAE^+$ ion. We have previously given evidence for the existence of two different geometries of this ion in the ground state: one, the most stable a n^{-1} configuration where the nitrogens are ionised and another one related to a configuration π^{-1}(9). The first one, n^{-1} is the most stable and corresponds to the adiabatic limit, owing to a charge delocalisation over the nitrogens, it involves thus a large reorganisation of the molecule. The second series, π^{-1} involves the removal of a π electron and can thus be easily reached from the valence $\pi\pi^*$ state, but it lies higher in energy. We have previously (10) found evidence for the interaction between these two configurations in the observation of the $TDMAE_n^+$ ion clusters. This results in surface crossings between the two ion configurations and autoionisation between the π^{-1} Rydberg series and the n^{-1} ion (6). We infer that one of these Rydberg states (R) of π^{-1} configuration is at play here and conveniently crosses surfaces V and Z. We surmise here that these V-R and R-Z intersections are very efficient and precede the V-Z intersection, hence the wavepacket is funnelled through this surface of R configuration . The present wavepacket movement initiated on the V surface passes efficiently to this Rydberg surface which is again traversed in 400 fs. The rapid torsional and pyramidalisation movements, initiated on the first surface likely directs the evolving system.

Also, the presently observed wavepacket movement is confirmed by another detection scheme with a 400 nm probe, in figure 4; here the probe laser has an energy much above the ionisation threshold. A similar group of

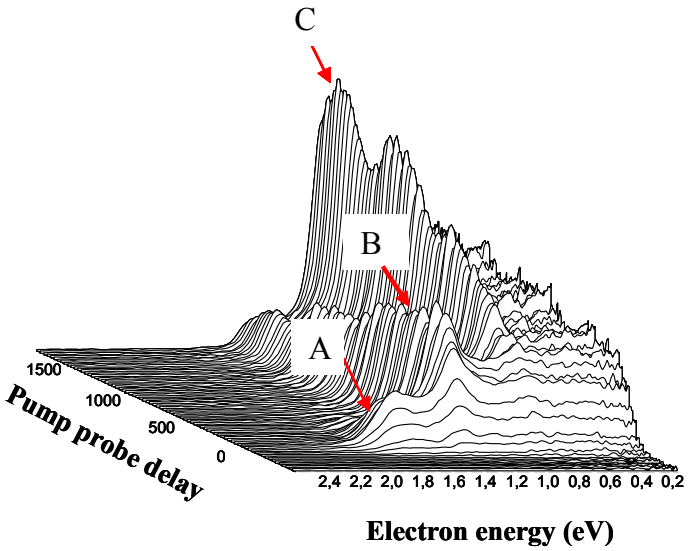


FIGURE 4: Radially integrated electron velocity images of TDMAE excited at 266 nm and ionised at 400 nm. Each curve corresponds to a pump/probe time delay.

bands B, C is observed at the same electron energies (2x800 nm photons have the same effect as 1x400 nm photon) which have the same decay pattern as before. The band at 1.6 eV corresponds to A' in figure 3 and has the same decay profile as A it bears thus the same label. Also, as for band A in figure 3 additional and weak shoulders can be seen on the high energy side of band A in figure 4, which appear with a shorter time evolution. These features could correspond to vibrations in the $TDMAE^+$ ion (0.2 eV). The different time behaviour should be indicative of the of the wavepacket motion in the V state probed more efficiently at lowest electron kinetic energies.

OSCILLATORY WAVEPACKET MOTION

Presently we have reported on the time evolution of the excited TDMAE molecule, as implicitly consisting of a damped motion, where the wavepacket created on the valence ππ* surface could be rapidly spread over the surface after passage of the conical intersections. This spreading should result from the gradients on the multidimensional energy surface, as seen for example on the lower part of the sketch in figure 2, after the passage close to the conical intersection.

Close inspection of figures 3,4 reveals an apparently different situation where peak C shows important modulations with a 500 fs period that increase in amplitude as time goes by.

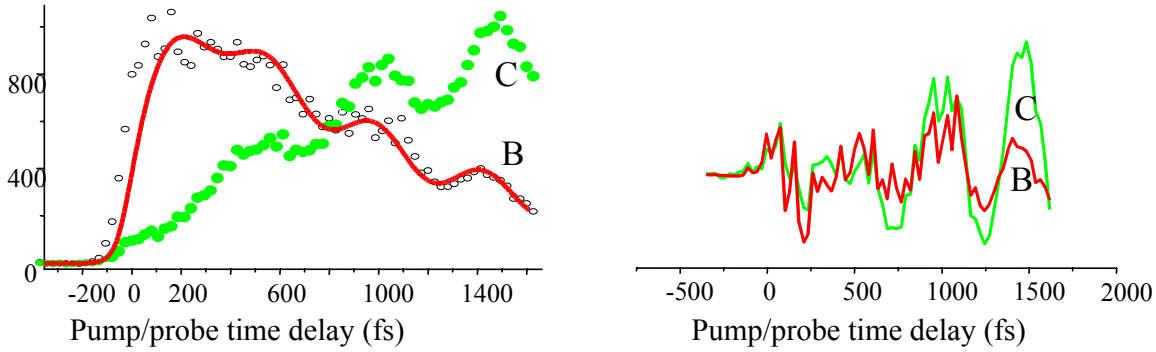


FIGURE 5: Left, time evolution of peaks B and C . Right : oscillatory part of these evolutions after subtraction of the exponential rises and decays.

Cuts of these bands have been made for bands B and C in figure 5. They are well simulated using simple exponential evolution combined with oscillatory behaviours. It is clearly evident that the oscillations increase within the 1500 fs time domain and this is independent from the decay of the B and C bands. These oscillations are in phase in B and C as shown in figure 5(right). We hence infer that the coherence is initiated by the passage of the wavepacket to the B and C potential energy surfaces and excitation occurs on a different coordinate than the "reaction coordinate"(11),(12). In the alternative case where the system would be trapped along the reaction coordinate, we could expect a different phase for the old and the new configurations since these two could be detected at different times/locus on the potential surfaces as plausibly for DABCO (13). The oscillatory movements for TDMAE occur then likely on a perpendicular coordinate to the evolution of the decay. The oscillations must have been set by the passage through (or near by) the crossings on the potential energy surface where the intermodal couplings should be the strongest.

CONCLUSIONS

Photoelectron imaging has revealed the existence of a short lived (400 fs) intermediate state in the relaxation pathway of valence (ππ*) excited TDMAE. This state has been provisionally assigned to a Rydberg π^{-1} state and should be a key transient in the electronic relaxation mechanism of these ethylene like molecules. The relaxation of electronically excited states should often be mediated by the passage through surfaces of Rydberg character

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